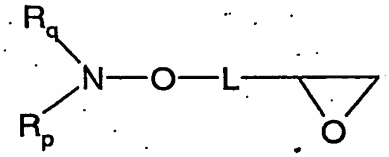
Claims

1. Method for the preparation of a comb or star copolymer comprising

a) polymerising in a first step one or more epoxy group containing monomers to obtain a polyether, wherein at least one monomer is of formula (I)



(I)

wherein L is a linking group selected from the group consisting of C_1-C_{18}alkylene, phenylene, phenylene-C_1-C_{18}alkylene, C_1-C_{18}alkylene-phenylene, C_1-C_{18}alkylene-phenylene-oxy and C_5-C_{12}cycloalkylene;

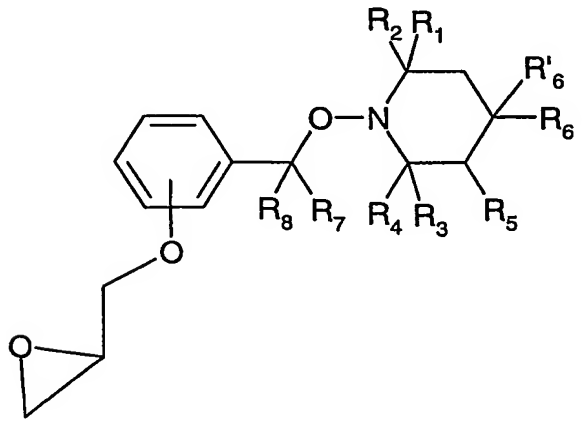
R_p and R_q are independently tertiary bound C_4-C_{28}alkyl groups which are unsubstituted or substitituted by one or more electron withdrawing groups or by phenyl; or

R_p and R_q together form a 5 or 6 membered heterocyclic ring which is substituted at least by 4 C_1-C_4alkyl groups and which may be interrupted by a further nitrogen or oxygen atom; and in a second step

b) adding to the polymer obtained in step a) at least one ethylenically unsaturated monomer, heating the resulting mixture to a temperature where cleavage of the nitroxylether bond occurs and radical polymerization starts;

and polymerizing to the desired degree.

2. A process according to claim 1 wherein the monomer is of formula (II)



(II) wherein

R_1, R_2, R_3 and R_4 are independently of each other C_1-C_4alkyl;

R_5 is hydrogen or C_1-C_4alkyl;

R'_6 is hydrogen and R_6 is H, OR_{10}, $NR_{10}R_{11}$, -O-C(O)-R_{10} or NR_{11}-C(O)-R_{10};

R_{10} and R_{11} independently are hydrogen, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, C_2-C_{18}alkinyl or C_2-C_{18}alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2-C_{12}alkylene bridge or a C_2-C_{12}-alkylene bridge interrupted by at least one O atom;or

R_6 and R'_6 together are both hydrogen, a group =O or =N-O-R_{20} wherein

R_{20} is H, straight or branched C_1-C_{18}alkyl, C_3-C_{18}alkenyl or C_3-C_{18}alkinyl, which may be unsubstituted or substituted, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;

C_5-C_{12}cycloalkyl or C_5-C_{12}cycloalkenyl;

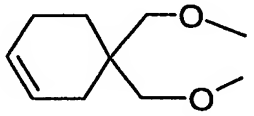
phenyl, C_7-C_9phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1-C_8alkyl, halogen, OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;

-C(O)-C_1-C_{36}alkyl, or an acyl moiety of a α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, -CO-NH-R_2, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+, ammnonium or an alkali metal cation; or

R_6 and R_6' are independently –O-C_1-C_{12}alkyl, -O-C_3-C_{12}alkenyl, -O-C_3-C_{12}alkinyl, -O-C_5-C_8cycloalkyl, -O-phenyl, -O-naphthyl, -O-C_7-C_9phenylalkyl; or

R_6 and R'_6 together form one of the bivalent groups -O-C(R_{21})(R_{22})-CH(R_{23})-O-, -O-CH(R_{21})-CH_{22}-C(R_{22})(R_{23})-O-, -O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-, -O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-, -O-o-phenylene-O-, -O-1,2-cyclohexyliden-O-,

-O--CH_2-CH=CH-CH_2-O- or  ; wherein

R_{21} is hydrogen, C_1-C_{12}alkyl, COOH, COO-(C_1-C_{12})alkyl or CH_2OR_{24};

R_{22} and R_{23} are independently hydrogen, methyl ethyl, COOH or COO-(C_1-C_{12})alkyl;

R_{24} is hydrogen, C_1-C_{12}alkyl, benzyl, or a monovalent acyl residue derived from an aliphatic, cycloaliphatic or aromatic monocarboxylic acid having up to 18 carbon atoms; and

R_7 and R_8 are independently hydrogen or C_1-C_{18}alkyl.

3. A method according to claim 2 wherein R_1, R_2, R_3, R_4 are methyl, or R_1 and R_3 are ethyl and R_2 and R_4 are methyl, or R_1 and R_2 are ethyl and R_3 and R_4 are methyl.

4. A method according to claim 2 wherein R_5 is hydrogen or methyl.

5. A method according to claim 2 wherein
R'_6 is hydrogen and R_6 is H, OR_{10}, $NR_{10}R_{11}$, -O-C(O)-R_{10} or NR_{11}-C(O)-R_{10};
R_{10} and R_{11} independently are hydrogen, C_1-C_{18}alkyl, C_2-C_{18}alkenyl, C_2-C_{18}alkinyl or C_2-C_{18}alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2-C_{12}alkylene bridge or a C_2-C_{12}-alkylene bridge interrupted by at least one O atom; or
R_6 and R'_6 together are both hydrogen, a group =O or =N-O-R_{20} wherein
R_{20} is H or straight or branched C_1-C_{18}alkyl.

6. A method according to claim 2 wherein
R_6 and R'_6 together form one of the bivalent groups -O-C(R_{21})(R_{22})-CH(R_{23})-O-, -O-CH(R_{21})-CH_{22}-C(R_{22})(R_{23})-O-, -O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-, -O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O- and R_{21}, R_{22} and R_{23} have the meaning as defined in claim 2.

7. A method according to claim 1 wherein the epoxy group containing monomer different from formula I is selected from the group consisting of ethylene oxide, propylene oxide, 2,3-epoxypropyl-phenylether, 2,3-epoxypropyl-4-nonyl-phenylether, epichlorohydrine and 2,3-epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether.

8. A method according to claim 1 wherein in Stepp a) the weight ratio of the monomer of formula I to the sum of the other monomers is from 99:1 to 1:99.

9. A method according to claim 1 wherein in step b) the ethylenically unsaturated monomer or oligomer is selected from the group consisting of styrene, substituted styrene, conjugated dienes, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides and vinylidene halides.

10. A method according to claim 9 wherein in step b) the ethylenically unsaturated monomers are styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, acrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

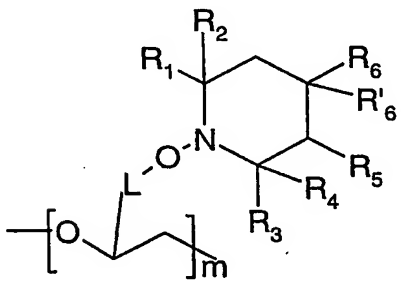
11. A method according to claim 1 wherein in step b) the weight ratio between the polyether prepared in step a) and the ethylenically unsaturated monomer is from 90:10 to 10:90.

12. A method according to claim 1 wherein in step b) the polymerization temperature is from 80° C to 160° C.

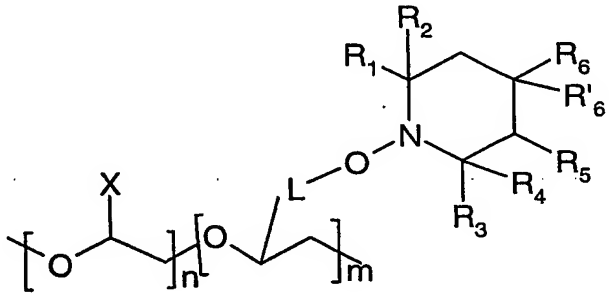
13. A composition comprising a compound of formula II as defined in claim 2, at least one epoxy functional monomer different from that of formula II and optional water or an organic solvent or mixtures thereof.

14. A polyether obtainable according to step a) of the method of claim 1.

15. A polyether having a repetitive strucural element of formula IIIa or IIIb



IIIa,



IIIb

wherein R_1, R_2, R_3, R_4, R_5, R_6, R'_6 and L are as defined above, m and n are number from 10 to 1000 and

X is H, CH_3, CH_2-O-C_6H_5, CH_2-O-C_6H_5-C_9H_{19}, -CH_2Cl or CH_2-O-CH_2-$(CF_2)_3CHF_2$.

16. A comb or star copolymer obtainable according to the method of claim 1.

17. A comb or star copolymer according to claim 16 wherein the ethylenically unsaturated monomer forming the comb or star is selected from the group consisting of styrene, substituted styrene, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles and (alkyl)acrylamides.

18. Use of a polyether with pending nitroxylether groups according to claim 15 for the preparation of a comb or star copolymer.

19. Use of a comb or star copolymer obtainable according to the method of claim 1 as adhesive, surface modifier, surfactant or compatibilizer in thermoplastic, elastic or thermosetting polymers or as plastic material for extrusion or injection molding for shaping parts.